HYDROGEN ABSORBING ALLOY AND SECONDARY BATTERY

CROSS-REFERENCE TO RELATED APPLICATIONS

This is a Continuation Application of PCT Application No. PCT/JP99/07318, filed Dec. 27, 1999, which was not published under PCT Article 21(2) in English.

BACKGROUND OF THE INVENTION

1. Field of the Invention

The present invention relates to a hydrogen absorbing alloy, a secondary battery comprising a negative electrode containing a hydrogen absorbing alloy, a hybrid car and an electric automobile, each of said hybrid car and electric automobile comprising a secondary battery comprising a negative electrode containing a hydrogen absorbing alloy.

2. Description of the Related Art

A hydrogen absorbing alloy, which is an alloy capable of storing hydrogen as an energy source easily and safely, attracts increasing attention as a new energy conversion material and as a new energy storage material. The use of a hydrogen absorbing alloy as a functional material is proposed in various fields. For example, it is proposed to use a hydrogen absorbing alloy for storage and transportation of hydrogen, for storage and transportation of heat, for heat-mechanical energy conversion, for separation and refining of hydrogen, for separation of hydrogen isotopes, for batteries using hydrogen as an active material, as a catalyst in synthetic chemistry, and as a temperature sensor.

Particularly, a hydrogen absorbing alloy capable of reversibly absorbing-desorbing hydrogen is widely used in the negative electrode included in a secondary battery. As a matter of fact, some kinds of secondary batteries of this type have already been put to practical use. Incidentally, secondary batteries are widely used as a power source for portable electronic appliances, since they are small and lightweight. Vigorous studies are being made nowadays in an attempt to improve the performance and the function of portable electronic appliances and to further miniaturize them. In order to make it possible to operate such a portable electronic appliance over a long time, it is necessary to increase the discharge capacity of the secondary battery per unit volume. Also, together with increasing the discharge capacity per unit volume, it is required in recent years to decrease the weight of secondary batteries, i.e., to increase the discharge capacity per unit weight.

An AB_5 type rare earth series hydrogen absorbing alloy reacts with hydrogen under room temperature and atmospheric pressure and is relatively high in chemical stability. Thus, extensive research is being made in an attempt to use the AB_5 type rare earth series hydrogen absorbing alloy as a hydrogen absorbing alloy for a battery. As a matter of fact, the AB_5 type rare earth series hydrogen absorbing alloy is actually used in the negative electrode included in secondary batteries available on the market. However, the discharge capacity of the secondary batteries available on the market, which comprise a negative electrode containing AB_5 type rare earth series hydrogen absorbing alloy, has already reached 80% of the theoretical capacity, making it difficult to further increase the discharge capacity of a secondary battery.

There are many rare earth-Ni series intermetallic compounds other than the AB_5 type referred to above. For example, it is disclosed in "Mat. Res. Bull., 11, (1976) 1241" that an intermetallic compound containing a rare earth element in an amount larger than that in the AB_5 type rare earth series intermetallic compound is capable of absorbing a larger amount of hydrogen at about room temperature, compared with the AB_5 type rare earth series intermetallic compound. Also, a hydrogen absorbing alloy in which a site A is a mixture of a rare earth element and Mg is disclosed in two publications. Specifically, a hydrogen absorbing alloy having a composition represented by $La_{1-x}Mg_xNi_2$ is disclosed in "J. Less-Common Metals, 73, (1980) 339". However, this hydrogen absorbing alloy has an excessively high stability with hydrogen and, thus, hydrogen is unlikely to be desorbed from the alloy, giving rise to the problem that it is difficult to desorb hydrogen when the secondary battery is discharged. A hydrogen absorbing alloy in which a site A is a mixture of a rare earth element and Mg is also disclosed in "Summary of lecture in the 120th Spring Meeting of Japan Metallic Society, P. 289 (1997)". Specifically, disclosed in this publication is a hydrogen absorbing alloy having a composition represented by $LaMg_2Ni_9$. However, this hydrogen absorbing alloy also gives rise to the problem that the hydrogen storage capacity is small.

A hydrogen absorption electrode containing a hydrogen absorbing alloy having a composition represented by $Mm_{1-x}A_xNi_aCo_bM_c$ is disclosed in Jpn. Pat. Appln. KOKAI No. 62-271348. On the other hand, a hydrogen absorption electrode containing a hydrogen absorbing alloy having a composition represented by $La_{1-x}A_xNi_aCo_bM_c$ is disclosed in Japanese Patent Disclosure No. 62-271349. However, the secondary battery comprising the hydrogen absorbing alloy disclosed in each of these Japanese Patent documents gives rise to the problem that the discharge capacity is low and the cycle life is short.

Also, a hydrogen absorption electrode containing a hydrogen absorbing alloy having a composition represented by general formula (i) given below and having a specified antiphase boundary is disclosed in Reissue Publication of International Patent Disclosure No. WO 97/03213 and U.S. Pat. No. 5,840,166. This hydrogen absorbing alloy has a crystal structure of $LaNi_5$, i.e., consists of a $CaCu_5$ type single phase:

$$(R_{1-x}L_x)(Ni_{1-y}M_y)_z \tag{i}$$

where R represents La, Ce, Pr, Nd or a mixture thereof, L represents Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Y, Sc, Mg, Ca or a mixture thereof, M represents Co, Al, Mn, Fe, Cu, Zr, Ti, Mo, Si, V, Cr, Nb, Hf, Ta, W, B, C or a mixture thereof, the atomic ratios x, y and z are respectively satisfy conditions of: $0.05 \leqq x \leqq 0.4$, $0 \leqq x \leqq 0.5$, and $3.0 \leqq z \leqq 4.5$.

The particular hydrogen absorbing alloy can be manufactured by uniformly solidificating a melt of the alloy having a composition represented by general formula (i) given above on a roll having a surface irregularity, in which the average maximum height is 30 to 150 μm, in a thickness of 0.1 to 2.0 mm under the cooling conditions that the supercooling temperature is 50 to 500° C. and the cooling rate is 1,000 to 10,000° C./sec, followed by applying a heat treatment to the solidificated molten alloy. It is taught that, if the manufacturing conditions fail to fall within the ranges noted above, the manufactured alloy is rendered to have a two phase structure consisting of crystal grains of the $LaNi_5$ type structure and crystal grains of the Ce_2Ni_7 type structure, resulting in failure to obtain the $LaNi_5$ type single phase structure.

However, a secondary battery comprising the negative electrode containing a hydrogen absorbing alloy having a composition represented by general formula (i) given above,